Minimising the global warming potential of clay based geopolymers

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Abstract

Production of Portland cement (PC) binders contributes substantially to global CO_2 production and various bodies including the Intergovernmental Panel on Climate Change (IPCC) have identified geopolymers as alternative binders with the potential to reduce these emissions. The hypothesis of this research is to investigate whether this is a realistic proposition in the light of limited waste materials such as fly ash and ground granulated blast furnace slag commonly used as geopolymer precursors. The effect of use of natural clay minerals as alternative precursors on global warming potential (GWP) is investigated. Methods of designing mixes with the lowest possible GWP are presented and these are compared to the GWP of PC and currently available metakaolin based geopolymer binders. It is concluded that it is possible to reduce the GWP by approximately 40 %, but other impacts may increase.

Highlights

- A life cycle inventory (LCI) for Metakaolin is presented
- A new methodology for geopolymer mix design is described
- A reduction in Global Warming Potential of approximately 40% is achievable
- The lowest Global Warming Potential can relate to the strongest mixes

1 Introduction

The Intergovernmental Panel on Climate Change (IPCC) has estimated that cement and ceramic manufacture is responsible for more than 20 % of the world's industrial carbon dioxide (CO_2) production (Metz, 2007). Substituting current concrete binders with geopolymers or high fly-ash and slag content binders were identified by the IPCC as realistic options for reducing these emissions. This paper describes an investigation into whether clay-based geopolymers have potential to decrease global CO_2 emissions and to consider how these reductions can be maximised.

The term "geopolymer" was first used for alkali-activated clay-based binders in the 1970s by French chemist Joseph Davidovits, but only since 2000 has there been concentrated international research into these novel binders. Most international research has focussed on geopolymers as an alternative to Portland Cement (PC) for concreting applications (Duxson et al., 2007), mainly because of significantly lower carbon dioxide equivalent emissions (CO_2-eq)(McLellan et al., 2011).

Geopolymers are formed by activating an aluminosilicate powder (precursor) with an alkaline hydroxide and/or silicate solution (activator). The precursors can come from a range of aluminosilicate sources with various ratios of aluminium (Al) and silicon (Si) and include natural clays and other natural minerals, calcined clays such as metakaolin and industrial by-products such as fly ash and slags.

The scientific literature has shown how the chemical composition of mixes containing metakaolin precursors and alkali silicate activators govern the final properties of hardened geopolymers (De Silva et al., 2007) and on how the GWP of geopolymer mixes of a

particular chemistry compare to those of PC (Yang et al., 2013), but there are no published studies on reducing the GWP of clay-based geopolymer mixes without changing the final mix chemistry.

As the alumiosilicate chemistry of geopolymers is fundamentally different to the calcium oxide based chemistry of PC binders, the vast majority of advances in reducing the impact of PC are therefore not applicable to geopolymers. The hypothesis presented in this paper is that the environmental impact, and specifically the GWP, of geopolymers can be substantially reduced without affecting the fundamental chemistry and therefore physical properties of the mixes.

1.1 Material quantities

Much of the original research into geopolymers was conducted on calcined clay-based precursors (Davidovits, 2011), but the focus of international research has subsequently moved to waste materials and by-products such as fly ash and slags which have more suitable flow characteristics for mass concrete applications (Duxson et al., 2007).

There is, however, insufficient fly ash and blast furnace slag produced worldwide to allow geopolymers based on these materials to replace a significant portion of global cementious binders. In 2006, the global cement requirement was 2540 Mt and this is projected to increase to 4350 Mt by 2050 (Schneider et al., 2011), as shown in Figure 1. Global fly ash from coal combustion is approximately 500 Mt / year (Ahmaruzzaman, 2010) and it has been estimated that only 55 % is suitable for use in blended PC binders (McCarthy et al., 2008). Approximately 242 Mt of iron slag is produced globally each year (Van Oss, 2013) and it was assumed for this analysis that 82 % of this will be granulated blast furnace slag (GGBS) suitable for binders (Euroslag, 2010). This means that less than 20 % of global cement requirements can currently be met by fly ash and slag, but this is likely to decrease below 10 % as cement demand increases and fly ash production decreases with moves from coal to more renewable forms of electricity production.

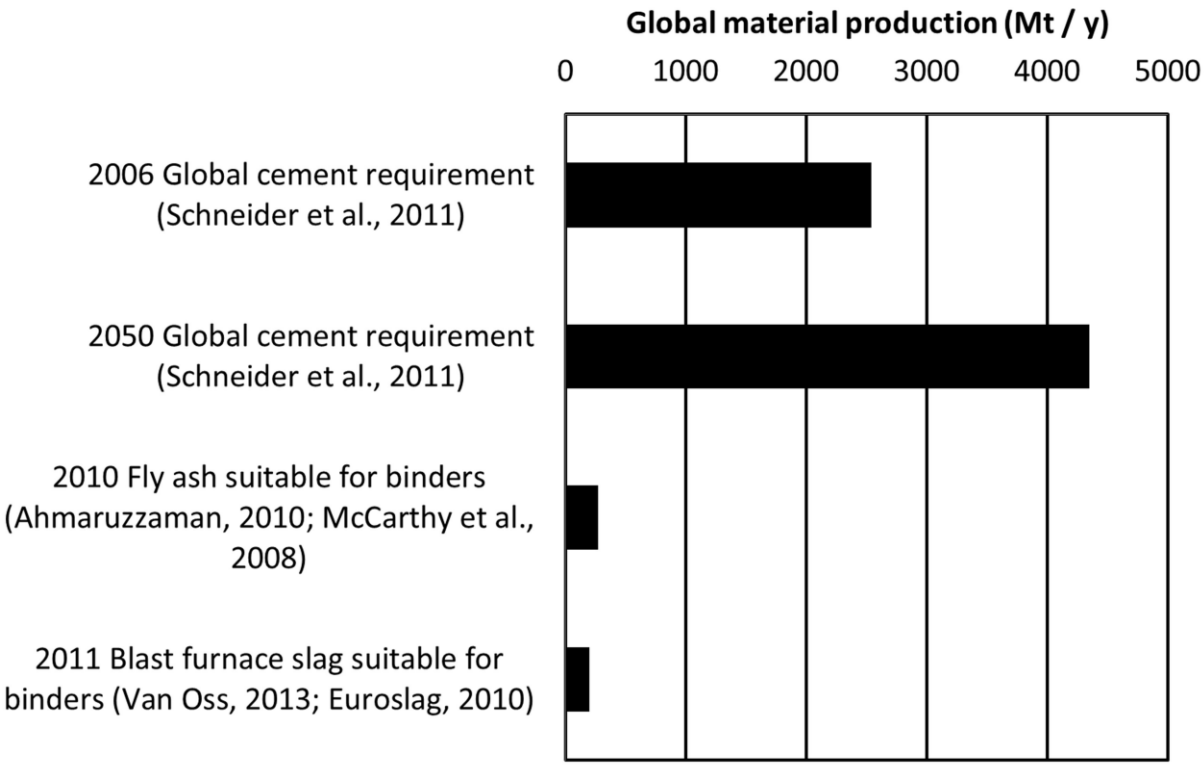

Figure 1: Global cement requirements and available resources

1.2 Focus of the paper

As shown in Figure 1, fly ash and blast furnace slag can replace a limited portion of existing or future cement requirements, and it is therefore be necessary to draw on reserves of geologically occurring minerals to meet future binder requirements.

This paper is focussed on clay based geopolymers as an alternate to PC in appropriate applications. Clay based geopolymers can have excellent strength and durability in the laboratory situation, but they require heat curing and high water contents to achieve the flow necessary for bulk concrete applications (Duxson et al., 2007). This paper is only considering clay based geopolymers in unreinforced prefabricated components (such as a replacement for concrete blocks, slabs and roof tiles) where lower flow is required and where better control of compaction and curing can be achieved.

This focus has numerous advantages:

- Design of clay based geopolymers can be done by targeting molar ratios of certain oxides, allowing easy comparison between mixes (Davidovits, 2011)
- Unreinforced precast PC concrete components are often heated to 60 - 80 °C (Won et al., 2013) which is a similar temperature to that for curing clay-based geopolymers, allowing direct comparison of curing conditions.
- Flow of material is less important for precast block/slab/ tile manufacture than for mass concreting applications as densification can be through external compaction and vibration.
- While global clay reserves have never been accurately quantified, it has been demonstrated that there is sufficient to replace binders for precast blocks in the UK

(Heath et al., 2013) and it is likely that a similar situation exists in many other countries.

1.3 System boundaries

There are a range of environmental risks associated with the production of cement and ceramics, including use of waste materials, primary resource use, embodied energy, embodied carbon and environmental toxicity which could be addressed through a full life-cycle assessment (LCA). Although additional impacts are considered, this paper is focussed on minimising global warming potential (GWP) to determine whether geopolymers are a realistic replacement for PC based binders as proposed by the IPCC (Metz, 2007). Throughout this paper, GWP is be presented as 100 y embodied CO_2-eq, according to the IPCC method (Solomon, 2007). Emissions data is from the EcoInvent life cycle inventory database focussed on western Europe, unless specified otherwise.

The system boundary for comparison of different technologies is from cradle to mixer, and therefore excludes mixing, moulding and curing, as illustrated in Figure 2. The raw materials and ancillaries used for production, energy consumption in production as well as emissions to air and water from production and an estimation of the impacts of establishing the infrastructure of the site are included. This allows comparison of the binder materials and allows calculation of the potential GWP saving from replacing PC based prefabricated components with clay based geopolymer prefabricated components.

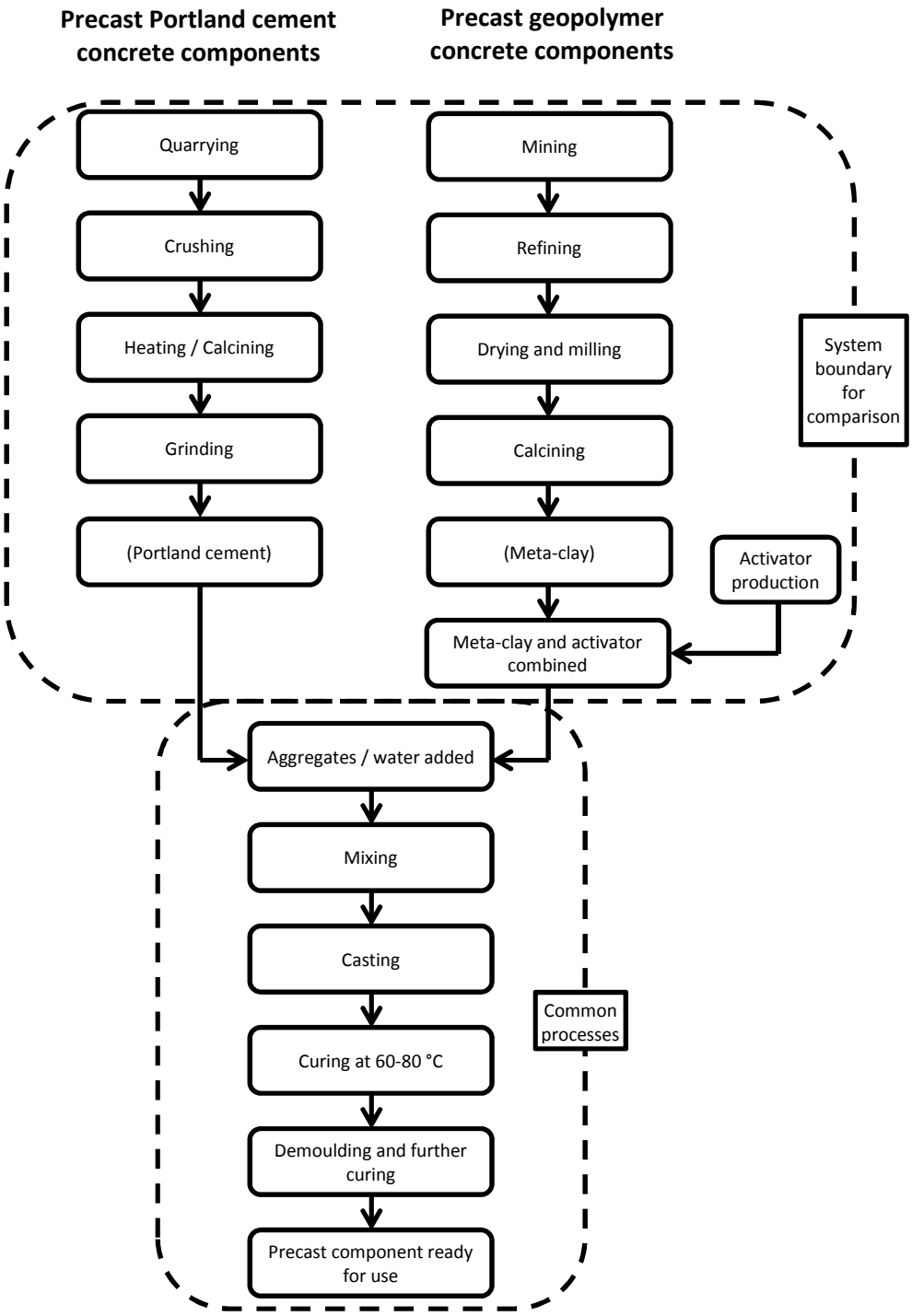

Figure 2: System boundaries for comparison

Although geopolymer properties can depend on curing temperature (Davidovits, 2011) the curing temperature was taken as the same as for PC components and the potential improved performance from higher temperature curing was not considered in order to simplify the analysis. The effect of strength was not directly considered in the analysis, but is discussed later in the paper. The results of this analysis should be considered with the system boundaries and assumptions in mind, and quantitative outputs should not be taken out of context.

2 Technology

When limestone is heated to form lime or cement, CO_2 is directly emitted from the carbonate in the limestone, but this does not occur when carbon-free natural clays are converted to meta-clays, potentially reducing GWP of geopolymer mixes. Meta-clay based geopolymers can include a range of precursors, but high purity kaolin which has been transformed into metakaolin by dehydroxylation, typically at 750 °C, is the most commonly used.

Davidovits (2011) recommends the following mix oxide molar ratios for meta-clay geopolymers with sodium or potassium hydroxide (NaOH or KOH) and silicate ($Na_2O.nSiO_2$ or $K_2O.nSiO_2$), activators, where M is either Na or K:

- $SiO_2:Al_2O_3$ = 3.5-4.5
- $M_2O:SiO_2$ = 0.20-0.28
- $H_2O:M_2O$ = 15.0-17.5
- $M_2O:Al_2O_3$=0.80-1.20

Although the presence of other elements such as calcium, magnesium and iron can affect geopolymer properties, the ratios presented above are most important in meta-clay based geopolymer mix design.

Kaolin is a clay mineral with a $SiO_2:Al_2O_3$ molar ratio of approximately 2:1 (Si:Al ratio of 1:1). For the manufacture of geopolymers, some soluble silica activator, normally in the form of sodium silicate, is used to increase the $SiO_2:Al_2O_3$ ratio from just over 2:1 in the metakaolin precursor to the target $SiO_2:Al_2O_3$ ratio. NaOH or KOH can then be added to obtain the desired $M_2O:SiO_2$ ratio without affecting the $SiO_2:Al_2O_3$ ratio. The use of sodium silicate and sodium hydroxide with metakaolin as a precursor has been the focus of much of the research and development into clay based geopolymers, but recent investigations have demonstrated the potential of other meta-clays in geopolymers.

Both illite and smectite (montmorillonite) are clay mineral groups with a naturally occurring $SiO_2:Al_2O_3$ ratio of approximately 4:1, and research has revealed it is possible to form geopolymers from calcined mixes of these clays (Seiffarth et al., 2013). Large quantities of these clay minerals are commercially extracted around the globe, often as mixed mineral bentonites which have high smectite contents.

Buchwald et al. (2009) demonstrated it is technically viable to produce geopolymers with smectite as the major mineral, although dissolution was slower than for metakaolin (approximately three times slower). The calcining temperature of 750 °C commonly used for metakaolin was found to produce high strength mixes for illite and smectite clays, and it was found that higher calcination temperatures resulted in undesirable more stable precursor phases. As illite and smectite based meta-clays naturally have $SiO_2:Al_2O_3$ ratios close to the target of 4:1, activation was with NaOH only. These alternative meta-clays are not currently available commercially, but similar technology to that required for metakaolin could be used for production.

3 Precursors

3.1 Clay minerals

The mining process for kaolin and smectite rich bentonite can vary from hydraulic mining to open pit extraction using draglines and other physical extraction techniques. The EcoInvent database does not include kaolin and bentonite with the same system boundary (bentonite is at the mine while kaolin is purified, dried and packaged and includes impacts of infrastructure). In order to simplify the analysis, it was assumed the bentonite had the same impacts as kaolin which is a conservative estimate. Kaolin mining in the UK (one of the locations considered for the EcoInvent database) produces large quantities of waste and historic hydraulic mining has led to high sediment levels in aquatic habitats (Thurlow, 2005), thereby increasing impacts relative to modern bentonite extraction.

3.2 Processing

There is little data on the processing of clays for use in geopolymers and this is an area where considerable research is required. Habert et al. (2011) produced the only Life Cycle Inventory (LCI) data for metakaolin in the peer reviewed scientific literature, based on data in the EcoInvent database and estimates of production impacts from a plant feasibility study in Canada (NLK, 2002). Whilst the LCI of metakaolin was not the principal focus of the Habert et al. paper, there were assumptions which call the reported GWP of 92.4 g CO_2-eq / kg metakaolin into question, particularly as this is well below the GWP of pure kaolin which has not had the additional high-temperature calcining phase (Figure 2).

The first assumption was that 1 kg of kaolin would form 1 kg of metakaolin, but because of mass loss during dehydroxylation, approximately 1.16 kg of kaolin are required to produce 1 kg of metakaolin if the calcination temperature is 750 °C (Chandrasekhar, 1996). The second questionable assumption is that the impacts for general clay extraction can be added to those from drying and calcining to obtain a figure for metakaolin. As mentioned earlier, hydraulic mining of kaolin can generate high levels of waste and increase sediment loads in surrounding aquatic environments, and these impacts and additional impacts of infrastructure development should be included.

For the purposes of this paper, the GWP of metakaolin was calculated by using 1.16 kg pure kaolin and adding gas heating of 2.5 MJ/kg metakaolin, as determined for a metakaolin plant feasibility study (NLK, 2002). This resulted in a 100 year GWP for metakaolin of 423 g CO_2-eq / kg metakaolin, nearly five times the value reported by Habert et al. but closer to the value of 330 g CO_2-eq / kg metakaolin reported by Jones et al. (2011) or 370 g CO_2-eq / kg presented by NLK (2002). The methodology used for the calculation of the GWP presented by Jones et al. (2011) is unclear, but the calculation by NLK (2002) included the use of waste bitumen as a secondary energy source which reduced the energy input requirements. This demonstrates the calculated value of 423 g CO_2-eq / kg metakaolin is reasonable.

As calcined bentonite (meta-bentonite) is not currently commercially available, there is no validated data on this available. The energy use for calcining kaolin was used for the bentonite, but an increased 1.21 kg bentonite was required to form the meta-clay, based on the increased loss on ignition shown in Table 1. This resulted in a 100 year GWP of 435 g CO_2-eq / kg.

3.3 Composition

A breakdown of the major minerals and oxides for relatively pure kaolin and metakaolin is presented in Table 1. The mineralogy for the plain kaolin was based on Greenwood et al. (2007), and the oxide composition for the kaolin and metakaolin were based on a commercially available metakaolin reported by Pacheco-Torgal et al. (2011), with the raw material oxide content back-calculated based on dehydroxylation of the kaolin only. It is assumed that quartz would remain unreactive even after calcining and is therefore not included in the oxide composition of the reactive portion.

The data for raw bentonite is based on the average of the values from six different bentonites sourced from the USA and Slovak Republic (Osacký et al., 2013). For the mixed mineral bentonite, the data for both the total material and for the reactive clay mineral fraction is presented. The three major clay mineral groups in the bentonite (smectite, illite and kaolinite) will largely dehydroxylated on heating to 750 °C and are assumed to participate in the geopolymerisation as demonstrated by Buchwald et al. (2009). Of the non-clay minerals, it was assumed that the feldspars would dehydroxylate to a reactive geopolymer precursor at temperatures below 750 °C (Xu and van Deventer, 2003), and that the quartz and opal-CT in the raw mix would be removed through a refining process similar to that used for kaolin.

Table 1: Clay precursors

Material	Kaolin	Metakaolin (reactive portion)	Bentonite	Bentonite meta-clay (reactive portion)
Major mineral groups (%)				
Smectite			87.3	
Kaolinite	88		0.7	
Illite			1.7	
Micas	9			
Feldspars	2		3.5	
Quartz	1		1.5	
Opal-CT			5.3	
Major oxide composition (%)				
SiO_2	44.8	49.8	55.4	63.4
Al_2O_3	38.2	43.5	15.2	19.7
Fe_2O_3	2.2	2.5	5.5	7.1
MgO	0.1	0.1	3.2	4.2
Na_2O	0.0	0.0	2.3	2.9
LOI	13.8*		16.9	
Global warming potential (gCO_2-eq/kg reactive meta-clay)				
GWP		423		435
* Back-calculated value, but with no effect on analysis				

4 Activators

Geopolymer activators are best described through molar ratios (Davidovits, 2011) and the analysis is therefore focussed on the GWP / mole of activator component. The activators of interest are sodium and potassium hydroxides and silicates.

4.1 Hydroxides

There a number of different methods of producing NaOH and KOH. NaOH is commonly manufactured using the chlor-alkali process. Chlorine gas is also produced in this process and the emissions distribution between the two products was done on a mass basis as the costs of chlorine and sodium hydroxide are constantly changing with demand, making allocation on an economic basis difficult. The NaOH production option with lowest GWP in the EcoInvent database is using a membrane cell. This was used in the analyses as it is currently the most common method of production and its global use is increasing relative to other methods (Gluszcz et al., 2013).

Another option for NaOH production is to react sodium carbonate (Na_2CO_3) with hydrated lime ($Ca(OH)_2$) to form two moles of NaOH and one mole unreactive calcite ($CaCO_3$). This has the advantage of both Na_2CO_3 and $Ca(OH)_2$ classified as irritants rather than the corrosive NaOH, so safety is improved. In other applications of NaOH, the presence of calcite may be undesirable, but as this is chemically similar to limestone aggregates commonly used in concretes, it is not anticipated to have a detrimental effect on performance. KOH can also be used as an activator component and this is manufactured using similar processes to NaOH.

4.2 Silicates

Both sodium and potassium silicates can be used for geopolymers, but because the majority of research and practice has concentrated on the use of sodium silicate which is lower cost and more freely available, only this will be analysed in this work. Furthermore, data on sodium silicate is available in the EcoInvent database.

There are five major commercial production routes for sodium silicate and these produce soluble silicates with different properties (Fawer et al., 1999). The general formula for sodium silicate is $Na_2O{\cdot}nSiO_2$ where n is the molar ratio. As the molar mass of Na_2O and SiO_2 is similar, the weight ratio (WR or modulus) is similar to the molar ratio. Of these, the major commercially available options have a WR between SiO_2 and Na_2O of either 2.0 or 3.3, although this can be changed through blending or addition of sodium hydroxide. The material with a WR of 3.3 is produced as dry furnace lumps which can be dissolved in water at elevated temperature to produce a liquor before use in geopolymers. WR 2.0 sodium silicate is produced as a 48% hydrothermal liquor which can be used directly as a liquid activator, or it can be spray dried to a soluble powder which does not require elevated temperature dissolution like the WR 3.3 solid.

It is possible to produce sodium silicate using lower impact methods (McGuire et al., 2011), but the methods above are currently the focus of industrial production in western Europe.

4.3 Amorphous silica

In addition to sodium and potassium silicates, there is potential to mix amorphous silica with NaOH or KOH. In the amorphous form, the silica is more easily dissolved in NaOH or KOH solution and this technique has been successfully used for meta-clay based geopolymer

production (Bernal-Lopez et al., 2011). A commonly used amorphous silica in PC concrete is silica fume which is a by-produce of the metallurgical silicon and ferrosilicon producing industries. Other forms of amorphous silica such as rice husk ash or ground waste glass were not considered as they are not as freely available in western Europe.

There is no information in the EcoInvent database on the GWP of silica fume, and little in the scientific literature. As silica fume can be considered a waste material, some previous studies have assigned no impact to it, in spite of processing required before use in binders. For this analysis, a GWP of 14 g CO_2-eq / kg was assigned to the silica fume if it was considered a waste material (no allocation of impacts), 120 g CO_2-eq / kg if allocation of GWP is by economic value and 700 g CO_2-eq /kg if allocation is according to mass, as determined by Grist et al. (2013). These were then increased to 15, 126 and 737 g CO_2-eq/kg for amorphous silica which represents 95.1% of the total (Bernal-Lopez et al., 2011).

For the majority of the analyses presented here, there is no allocation of impacts to the silica fume, other than those directly from processing and transporting the material. The effect of allocation of impacts is presented for some mixes to demonstrate the magnitude of allocation assumptions on outcomes. This paper is focussed on the effect of geopolymer mix design on global emissions and as allocation of emissions does not affect actual emissions so this approach is considered valid. It is also compatible with the data for blended PC from the EcoInvent database which allocates no emissions to fly ash or blast furnace slag.

In order to obtain an estimate of additional impact categories for a life cycle inventory, data from packaging cement materials and 50km of road transport was used to represent the “no allocation of impacts” situation for silica fume. This returns a similar GWP to that of Grist et al. (2013).

4.4 Activator GWP

A summary of the GWP of the different activator options is presented in Figure 3.

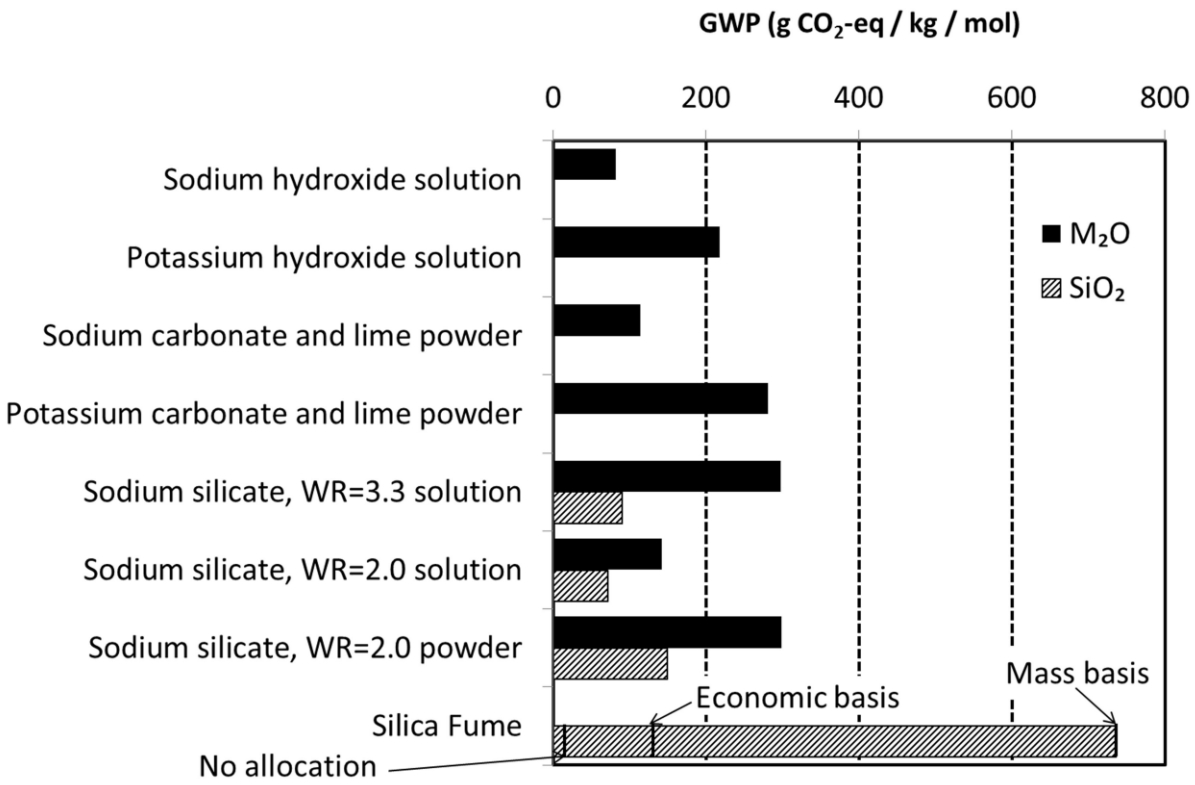

Figure 3: Summary of activator GWP with different allocation basis for silica fume

As shown in Figure 3, sodium hydroxide (NaOH) solution has the lowest GWP / mol M_2O of the activators considered. The safety benefits of using sodium carbonate and lime instead of sodium hydroxide should, however, be considered along with the GWP. The WR 2.0 sodium silicate hydrothermal liquor has the lowest GWP / mol SiO_2 for the sodium silicates, but the silica fume has considerably lower GWP / mol SiO_2 if no GWP from the production of silicon and ferrosilicon is allocated to it. If the GWP is allocated on either an economic or mass basis, the impacts increase to above that of the sodium silicate solutions.

Sodium hydroxide solution has the lowest GWP / mol M_2O and based on the assumptions of no allocation of impacts for the silica fume, this has the lowest GWP / mol SiO_2. However, the overall mix impacts will depend on both the activator and precursor impacts.

5 Production of meta-clay geopolymers

Theoretical mix designs and GWP for 1 kg of solid geopolymer binder, with molar ratios based on the mean of the range presented by Davidovits (2011), are presented in Table 4. The molar ratios listed at the end of the table are in the middle of the range recommended by Davidovits (2011) shown earlier. The water in the mixes is included for reference, but this is not included in the calculation of GWP as it is outside the system boundary for analysis shown in Figure 2. All mix proportions were calculated with a constraint that the mass of solids (particulate and dissolved) must be 1000g and that the molar ratios must be as listed at the end of the table.

Table 4: Options for 1 kg of geopolymer binder with identical key molar ratios

	Mix A		Mix B		Mix C	
	Mass (g)	GWP (g CO_2-eq)	Mass (g)	GWP (g CO_2-eq)	Mass (g)	GWP (g CO_2-eq)
Metakaolin	561.4	237 (39 %)	216.0	91 (17 %)	561.4	237 (55 %[1])
Bentonite meta-clay			671.5	292 (55 %)		
Sodium hydroxide 50% solution	129.0	66 (9 %)	290.5	149 (28 %)	367.9	189 (44 %[1])
Sodium silicate WR 3.3, 37% solution	1050.4	445 (59 %)				
Silica fume					296.1	4[1],37[2],218[3] (1[1],8[2],34 %[3])
Additional water	7.3		600.5		642.1	
Total	1000 (dry)	749 (100 %)	1000 (dry)	533 (100 %)	1000 (dry)	431[1],464[2],644[3] (100 %)

Mix molar ratios:
SiO_2:Al_2O_3 = 4.0; Na_2O:SiO_2 = 0.24; H_2O:Na_2O = 16.5; Na_2O:Al_2O_3 = 1.0
[1] No allocation of GWP to silica fume
[2] GWP allocated to silica fume on economic basis
[3] GWP allocated to silica fume on mass basis

Mix A used a metakaolin precursor and sourced activators from commercially available sodium hydroxide and WR3.3 sodium silicate sources, as currently practiced and presented in the LCA study by Habert et al. (2011) and the study on physical properties by De Silva and Sagoe-Crenstil (2008). As shown, sodium silicate provides the greatest contribution to GWP, and this should therefore be targeted when attempting to reduce GWP.

Mix B represents the minimum GWP that can be obtained with a commercially available sodium hydroxide activator, but with two precursors (metakaolin and bentonite meta-clay). This alternate meta-clay mix produces a saving of 29% in GWP through eliminating the need for sodium silicate. Even though the precursor GWP is higher than for Mix A, the overall GWP is lower and demonstrates the effect of considering the impact of the entire mix rather than just the precursor. As mentioned earlier, previous research with illite and smectite meta-clay geopolymers indicated dissolution is slower than for metakaolin based geopolymers (Buchwald et al., 2009), but this was not considered in the analysis presented here as mixing is outside the system boundary.

Mix C was designed to minimise the GWP by varying both the activators and precursors and allowing the use of silica fume as the soluble silica source. As noted by Bernal-Lopez et al. (2011), the NaOH must be mixed with silica fume and allowed to dissolve (for 24 hours in the study in question), but this initial mixing was not included in the calculation of GWP. The mix design contains activators with the lowest GWP per mole Na_2O and SiO_2 if it is assumed there was no allocation of GWP to the silica fume (Figure 3). If the same mix design was

used but a portion of the GWP from the production of metallurgical grade silicon and ferrosilicon alloys was allocated to the silica fume on either a mass or economic basis, the GWP increases and can be higher than Mix B, as shown in Figure 4, but still lower than that of Portland cement or Mix A which is the current practice with clay-based geopolymers.

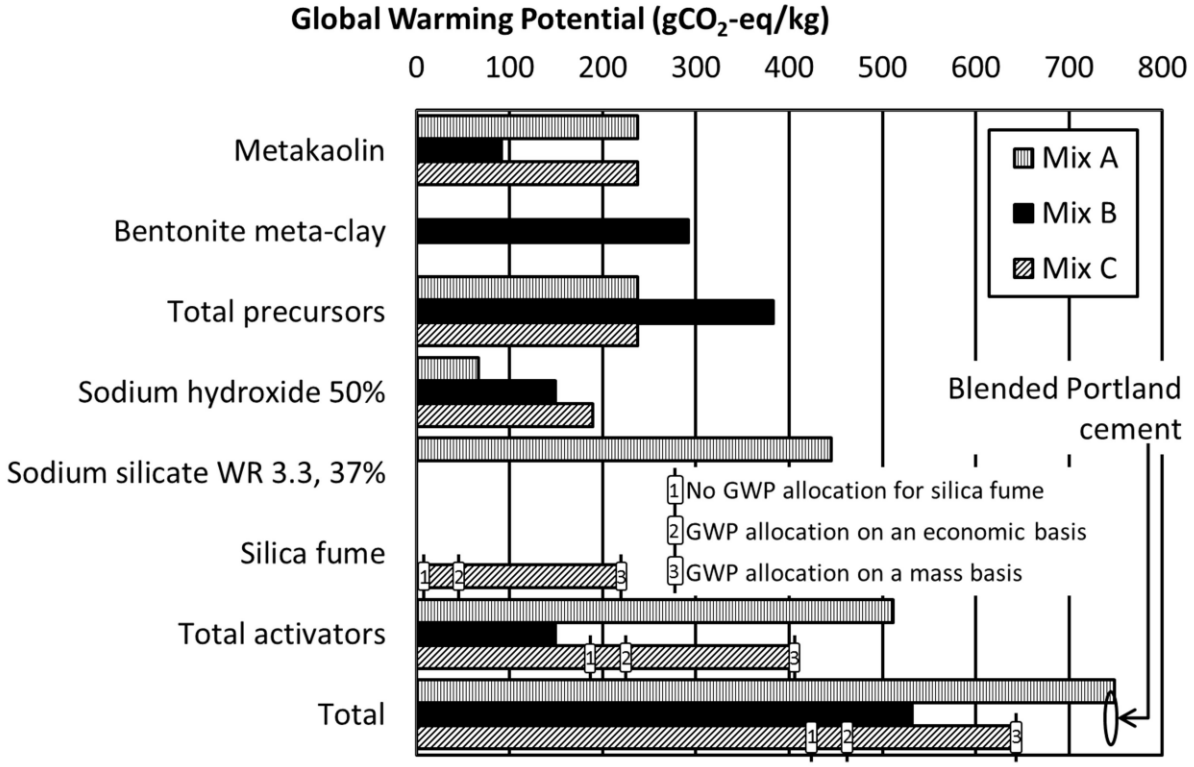

Figure 4: GWP of blended PC and chemically similar geopolymer mixes

As shown in Table 4 and Figure 4, there is considerable variation in the GWP of chemically identical binders, based on the selection of precursors and activators. From the data presented, it is clear that it is possible to reduce the GWP of a metakaolin based geopolymer considerably through activator choice. If a low GWP source of amorphous silica is not available, reductions in GWP can be obtained through the use of alternative meta-clay precursors which have a naturally occurring SiO_2:Al_2O_3 ratio closer to the target ratio of 4.0, thereby eliminating the requirement for sodium silicate.

From the analysis presented here, it is evident that the use of sodium silicate from the commercial sources described by Fawer et al. (1999) should be avoided if the intention is to reduce the GWP of meta-clay based geopolymers.

6 Factors influencing GWP

An optimisation process was undertaken to minimise the GWP of meta-clay geopolymers, while constrained by the mix design in a literature reference with a wide range of oxide ratios (De Silva and Sagoe-Crenstil, 2008). The “current practice” values presented in Table 5 are based on WR 3.3 sodium silicate, sodium hydroxide and metakaolin as in the original reference by De Silva and Sagoe-Crenstil (2008), while the potential values are based on the same oxide ratios but using either alternative alternate meta-clays or silica fume in

addition to metakaolin and sodium hydroxide to obtain the mix with lowest possible GWP. For the analysis presented here, it was assumed there was no allocation of GWP to silica fume. The ratios of SiO_2:Al_2O_3 and Na_2O:Al_2O_3 for the mixes is presented along with the GWP in Table 5. The percentage reduction in GWP is indicated in parenthesis. The quantity of water is not included in the calculation of GWP as it is outside the system boundary in Figure 2.

Table 5: GWP using current practice and potential reduction in GWP

SiO_2:Al_2O_3	Na_2O:Al_2O_3	GWP (g CO_2-eq / kg) and reduction from current practice (%)		
		Current practice[1]	Alternative meta-clays[2]	Silica fume[3]
3.81	0.263	743	542 (27 %)	448 (40 %)
3.00	0.333	696	565 (19 %)	506 (27 %)
2.50	0.400	660	585 (11 %)	551 (17 %)
5.01	0.333	837	575 (31 %)	458 (45 %)
2.50	0.333	638	561 (12 %)	526 (18 %)
3.00	0.234	662	526 (20 %)	462 (30 %)
3.00	0.467	736	612 (17 %)	559 (24 %)

[1] Using metakaolin, sodium hydroxide and WR 3.3 sodium silicate as in De Silva and Sagoe-Crenstil (2008)
[2] Using metakaolin, bentonite meta-clay and sodium hydroxide
[3] Using metakaolin, sodium hydroxide and silica fume (with no allocation of GWP)

As shown, it is possible to obtain GWP reductions of up to 45% for the geopolymer binders, but this reduction is highly dependent on the mix design. The Pearson rank-order correlation coefficients for factors influencing the GWP using current practice, alternate meta-clays and silica fume are presented in Table 6. The values indicate the relative strength of correlation and those significant at a 0.05 (95% confidence) and 0.01 (99% confidence) level are highlighted.

Table 6: Factors influencing GWP

Molar ratio	Unitless correlation coefficient between factor and GWP (correlation coefficient for reduction from current practice)		
	Current practice[1]	Alternative meta-clays[1]	Silica fume[1]
SiO_2:Al_2O_3	0.94**	-0.06 (0.95**)	-0.69 (0.94**)
Na_2O:Al_2O_3	-0.08	0.98** (-0.43)	0.86* (-0.47)

[1] Definitions as in Table 5
* Correlation is significant at the 0.05 level (2-tailed)
** Correlation is significant at the 0.01 level (2-tailed)

As shown, for the current practice of using metakaolin, sodium hydroxide and sodium silicate, only the SiO_2:Al_2O_3 ratio has a significant correlation with GWP at the 99% confidence level. This is unsurprising as the sodium silicate has the greatest GWP of all mix components (Table 4). The reductions in GWP that can be obtained by using either alternative meta-clays or silica fume are most strongly correlated with the SiO_2:Al_2O_3 ratio (significant at 0.01 level), and this effect is illustrated in Figures 5 and 6.

The Na_2O:Al_2O_3 ratio is correlated with the GWP of the alternative meta-clay and silica fume mixes at the 0.01 and 0.05 levels respectively. This is largely because there is a direct relation between the Na_2O:Al_2O_3 ratio and the quantity of activator added.

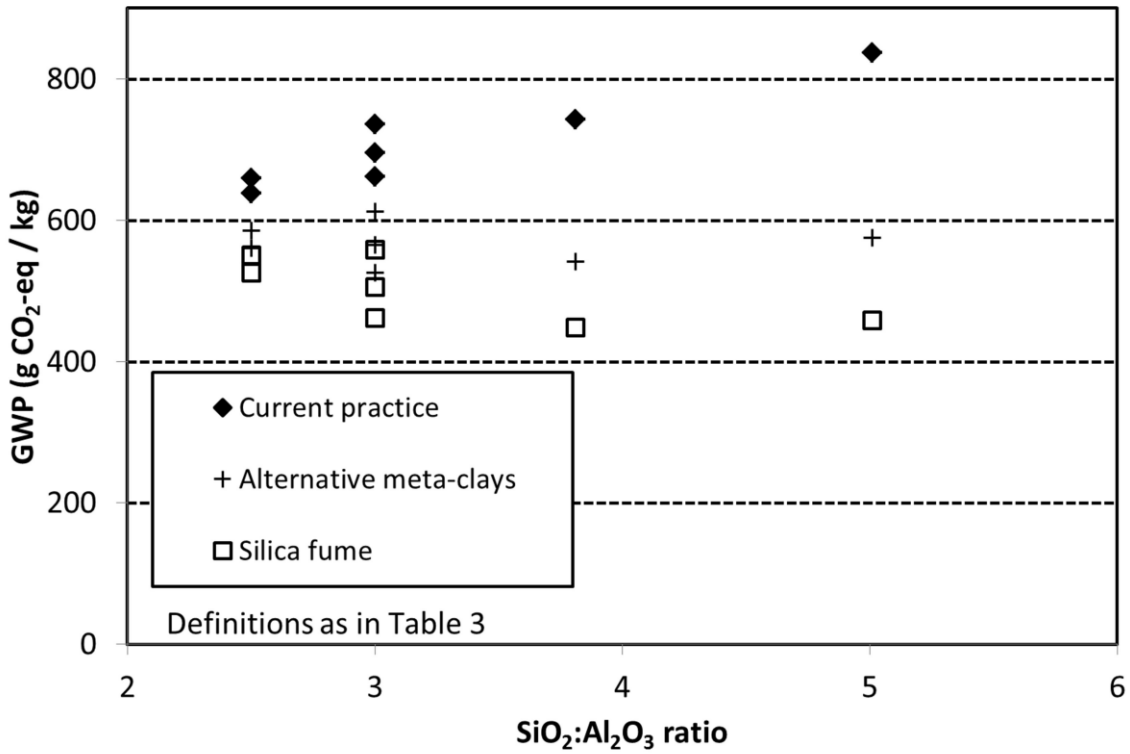

Figure 5: The effect of SiO_2:Al_2O_3 ratio on GWP

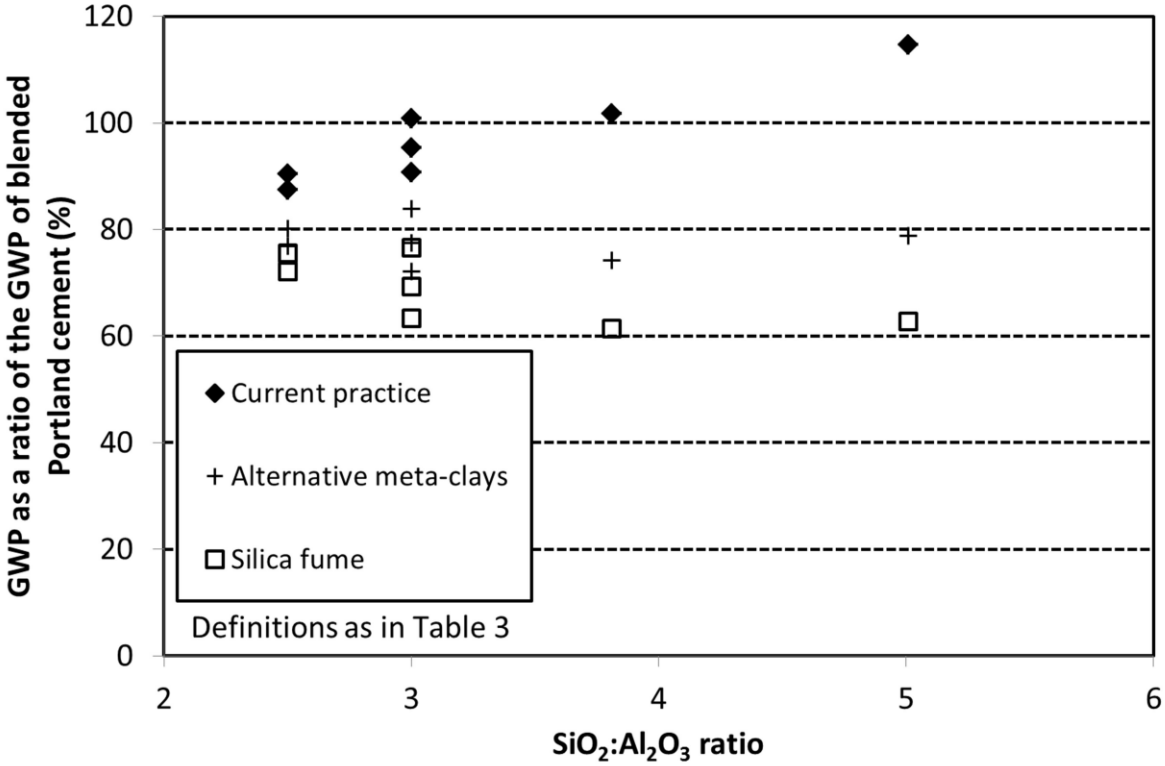

Figure 6: The effect of SiO_2:Al_2O_3 ratio on potential reduction in GWP

As shown in Figure 5, the higher SiO_2:Al_2O_3 ratios with current practice metakaolin based geopolymer binders have a similar GWP to PC binders, as noted by Habert et al. (2011). This previous work quantified the GWP the mixes using the current practice, but did not attempt to minimise GWP. The similarity with the common practice data presented here confirms the approach followed.

The mix with lowest GWP potential had a SiO_2:Al_2O_3 ratio of just below 4 which is an important outcome as experimental studies have shown a ratio of 3.5-4 provides the highest strength mixes for meta-clay based geopolymers (Duxson et al., 2005). The opportunity for maximum strength at the minimum GWP is unusual for construction materials and this should be utilised as far as possible for the mixes with alternate meta-clays and silica fume.

7 Discussion

7.1 Mechanical strength

The data presented above indicates clay-based geopolymer binders can have a much lower GWP than that of blended PC binders, provided the goal of minimising GWP is embedded in the mix design. The strength and durability of these mixes does, however need to be considered. Research into metakaolin based geopolymers activated with sodium hydroxide and amorphous silica has demonstrated strengths over 70MPa are achievable for an optimum SiO_2:Al_2O_3 ratio of approximately 3.8 (Duxson et al., 2005) which is similar to that for a Portland cement paste (Chindaprasirt et al., 2005). Figure 6 shows that using the methodology presented here, with this SiO_2:Al_2O_3 ratio there is potential for a GWP approximately 40% lower than a blended Portland cement paste. Curing at 60-80 °C results in metakaolin based geopolymers having rapid strength gain, where the two day strength is similar to 28 days strength (Rovnaník, 2010) which is desirable for precast concrete units. A comparison between the geopolymer and PC binders for precast units on a similar strength basis is therefore reasonable.

7.2 Environmental impacts of meta-clays

Meta-clays, and in particular metakaolin are used in both geopolymer and PC based binders, but there is a lack of rigorous data in the peer-reviewed literature for the environmental impact of this material. By analysing the processes for conversion of kaolin to metakaolin, it is possible to provide a reasonable estimate for the environmental impacts of the production of these meta-clays. The factory gate data for the 10 impact categories (including 100 year GWP) for the CML 2 baseline method is presented in Table 7 for a bentonite meta-clay and metakaolin using natural gas-based heating as is common in current commercial production (Thurlow, 2005). It may be possible to reduce these impacts by using alternate heat sources (e.g. biomass heat), this is not currently common practice but should be considered in future plant design or retrofit. Without validation against actual production processes, the data for which is not available in the public domain, these figures should be considered reasonable estimates of impacts.

Table 7: CML2 baseline method impacts per kg meta-clay

Impact category	Unit	Meta-bentonite	Metakaolin
Abiotic depletion	kg Sb eq	3.48E-03	3.39E-03
Acidification	kg SO_2 eq	1.07E-03	1.03E-03
Eutrophication	kg PO_4 eq	6.72E-05	6.47E-05
GWP (100 year)	kg CO_2 eq	0.434	0.421
Ozone layer depletion	kg CFC-11 eq	4.07E-08	3.98E-08
Human toxicity	kg 1,4-DB eq	0.0717	0.0694
Fresh water aquatic ecotox.	kg 1,4-DB eq	7.55E-03	7.21E-03
Marine aquatic ecotoxicity	kg 1,4-DB eq	33.6	32.4
Terrestrial ecotoxicity	kg 1,4-DB eq	9.07E-04	8.66E-04
Photochemical oxidation	kg C_2H_4	5.41E-05	5.20E-05

7.3 Potential reduction in GWP

Numerous research programmes have been conducted into minimising the GWP of Portland cement based binders and the majority of these studies have focussed on blends with high fly ash and GGBS contents, which were identified by the IPCC as one of two technologies with the potential to significantly reduce the GWP of concrete manufacture (Metz, 2007). A recent study into the GWP of PC based mixes with high GGBS contents (Feiz et al., 2014) indicated that it is possible to reduce the GWP of Portland cement based binders by 65 % compared with the reference value used for this current study. This exceeds the 40 % reduction in GWP claimed here, but the 65 % reduction in GWP was achieved by replacing 70 % of the Portland cement clinker with GGBS and considering the GGBS as a waste and therefore allocating no GWP to it.

While a 70% replacement with GGBS is possible for certain projects, it is an unrealistic proposition on a global scale considering the availability of GGBS shown in Figure 1. To achieve the approximately 40 % reduction in GWP demonstrated for geopolymers in this current study, the work by Feiz et al. (2014) used a GGBS content of 45 %, but even this is well beyond the current GGBS availability of below 8 % of global binder requirements. This indicates that while PC based mixes with high GGBS contents can contribute to a reduction in GWP, the poor availability of the GGBS means the impact will be limited.

7.4 Broader environmental impacts

While this paper has focussed on minimising the GWP, the broader environmental impacts of clay-based geopolymers should also be considered. The three mixes in Table 4 are compared with a blended PC binder in Figure 7 where each of the CML 2 baseline impact categories is presented as a percentage of the value for a blended PC binder.

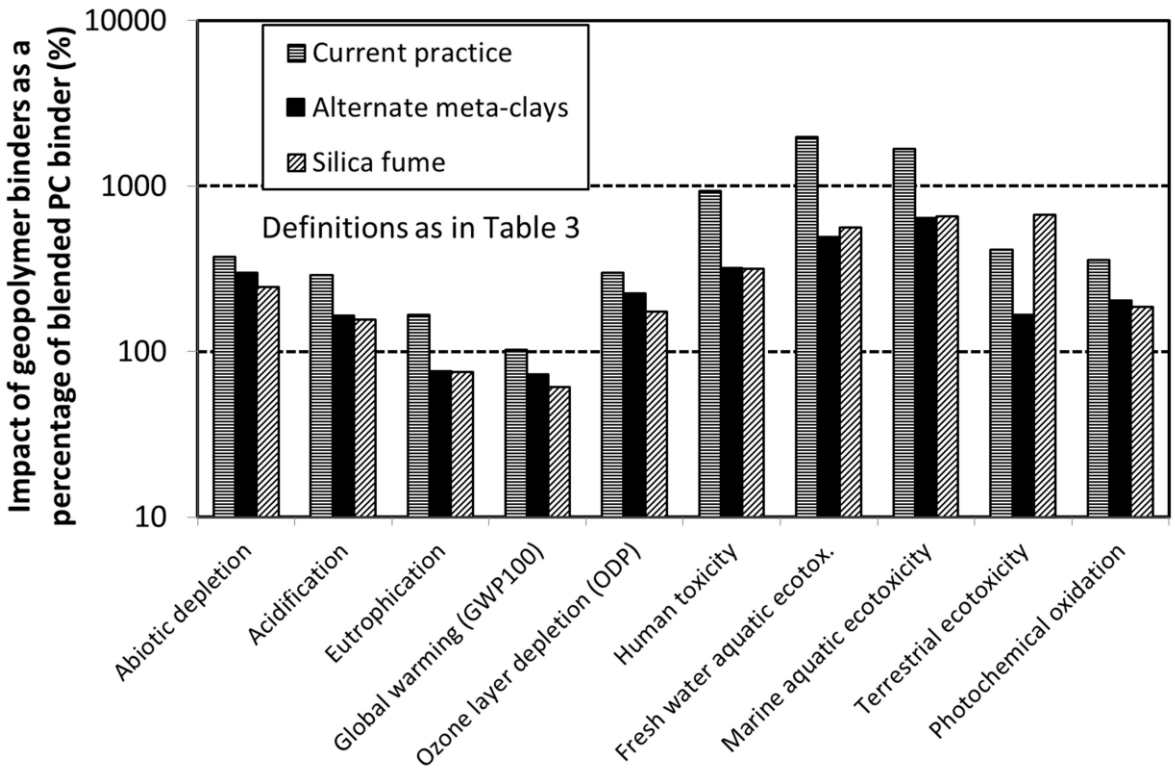

Figure 7: Impacts of geopolymer binders as a percentage of a blended PC binder

Mix A (current practice) has a similar GWP to the blended PC, but has increased impacts in all other categories. This implies that there is little environmental benefit to moving from blended PC mixes to metakaolin mixes where sodium hydroxide and WR 3.3 sodium silicate are used as activators. In order to achieve the goal of a reduction in GWP, a new approach is required and the approaches investigated as part of this paper were to use either alternate sources of clay where the natural ratio of SiO_2:Al_2O_3 in the clay is closer to the desired mix ratio, or to use a lower impact source of soluble silica. Both of these can result in a meta-clay based geopolymer binder GWP significantly below that of a blended PC binder.

Mix B (alternate meta-clays) has impacts below that of Mix A in all categories, but is only below the blended PC in two categories, one of which is GWP. Mix C with silica fume as the source of soluble silica has lower impacts than Mix B in six of the ten categories (including GWP), but has increased impacts in the remaining four. It is only below a blended PC in two categories where the major reduction is in GWP. An evaluation of the relative importance of the different impact categories is beyond the scope of this paper, but the GWP of PC production has been identified as a serious environmental concern which needs to be addressed (Metz, 2007). The methodology presented here could equally be applied to any impact category, or even the cost of the binder.

8 Conclusions

The analysis in this paper has demonstrated that geopolymers based on clays can play a role in reducing global CO_2 emissions from Portland cement manufacture. There is insufficient fly ash and blast furnace slag produced annually to meet global binder requirements and natural clays could be utilised to meet future binder demand. Clay based geopolymers are more suitable for precast and masonry unit production as the flow characteristic of these materials and heating required can make them unsuitable for general

concreting applications, and the comparisons in this paper are based on these precast geopolymer components with soluble SiO_2:Al_2O_3 ratios of 3.5-4.0:1 in the binders. When subjected to heat curing, these mixes can have comparable strength to blended PC binders.

Reductions in approximately 30% in GWP can be achieved if PC based binders are replaced with bentonite based meta-clay geopolymer precursors, and activators chosen with a view to reduce GWP. Using smectite rich bentonite as a meta-clay source has potential to reduce GWP significantly, and this area requires detailed scientific investigation. These materials are not currently commercially available in large quantities, and limited previous experimental studies have shown that these materials may require different manufacturing processes as precursor dissolution is slower than for metakaolin geopolymers.

Geopolymers based on only metakaolin precursors can have a lower GWP than PC based binders, but they are unlikely to provide large reductions in GWP unless a secondary precursor or activator with high soluble silica content and low GWP, such as silica fume, can be used. Using silica fume as the silica source with a metakaolin precursor can result in GWP reductions of approximately 40% if silica fume is assigned no impacts from the production of silica fume and ferrosilicon. Further research into the impacts of silica fume and other amorphous silica materials should be conducted so there is improved confidence in the environmental benefits of using these materials.

The SiO_2:Al_2O_3 ratio is the most important factor controlling GWP for both metakaolin and bentonite meta-clay geopolymers. The lowest GWP can be achieved for mixes with SiO_2:Al_2O_3 ratios in the range of 3.5-4.0:1, which corresponds to ratios which provide highest strength.

The hypothesis that it is possible to provide significant reductions in the GWP of clay-based geopolymers without affecting their chemical composition and therefore mechanical performance has been conclusively proven. The use of multiple precursors, activators and curing temperatures for geopolymer manufacture can lead to complex mix design, but has the potential to reduce the GWP potential to a level well below that of “just add water” Portland cement. It can therefore be concluded that the recommendation of the IPCC that PC binders be replaced by geopolymers in suitable applications can result in a decrease in global CO_2 emissions, but there may be increased impacts in some other environmental impact categories which should be considered before use.

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